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Special Report

HEAT OF FORMATION OF Li_3AlH_6 (C)

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TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

ABSTRACT

The heat of formation of a material, Li_3AlH_6, (synthesized at Reaction Motors) has been determined in this laboratory by measuring the heats of reaction of aluminum, lithium, and Li_3AlH_6 in 4 N HCl at 25°C in a closed bomb.

The heats of solution were found to be:

	$\Delta H_{298°}$ kcal/mole
Aluminum	-128.14 ± 0.39
Lithium	-67.05 ± 0.53
Li_3AlH_6	-249.90 ± 1.47

From this data, the heat of formation of Li_3AlH_6 was calculated to be:

$$\Delta Hf_{298°} Li_3AlH_6 = -79.4 \pm 3.4 \text{ kcal/mole}$$

INTRODUCTION

Recently, Reaction Motors Division of Thiokol Chemical Corporation has successfully synthesized a compound which, upon analysis, appears to be Li_3AlH_6. A sample of this material was received from Reaction Motors for thermochemical study in an attempt to determine its heat of formation.

The method employed was that of measuring the heats of solution of aluminum, lithium, and Li_3AlH_6 in 4 N HCl, from which the heat of formation of the compound was calculated.

Although the aluminum and lithium data, and a description of the apparatus were reported in an earlier report[1], they are repeated here for the convenience of the reader.

APPARATUS

The calorimeter is described in detail in Appendix I. It consists essentially of an adiabatically-operated Parr combustion calorimeter, modified to increase its sensitivity. The temperature sensing element is a thermistor in a Wheatstone bridge network with a sensitivity of 6.8×10^{-5} °C or 0.17 calories. Under adiabatic conditions the thermal leak rate is 7×10^{-5} deg. $min.^{-1}$. The reaction was carried out in a bomb in which the liberated hydrogen was confined.

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[1] Special Report, "Heat of Formation of $LiAlH_4$," National Research Corporation, April 1963, Nonr - 3608(00)

MATERIALS

The following materials were used in this work:

Material	Source	Purity
Aluminum	Mallinkrot Chemicals	99.9%
Lithium	Lithium Corporation of America	99.9%
Li_3AlH_6	Reaction Motors Division, Thiokol Chemical	92.87%

The analyses of these materials are shown in Appendix II.

EXPERIMENTAL

One-hundred fifty ml of 4 N HCl was added to the bomb. To this was added 4 drops (0.17 gm) of 10% platinum chloride solution as a catalyst to hasten the reaction rates.

The samples were sealed under argon in glass ampoules. A dry box was used for preparation of the lithium and the Li_3AlH_6 samples. The sample-containing ampoule was placed in the bomb, the lid put in place, and the air exhausted from the bomb. Argon was allowed to replace the air. This procedure prevented the possible ignition of the hydrogen-oxygen mixture which would be present during and after a run. The omission of this step resulted in a hydrogen-oxygen combustion in an early run.

The bomb was placed in the calorimeter bucket and 2000 ml of distilled water added. The bucket and jacket temperatures were adjusted to 24.85°C to 25.00°C. Upon reaching equilibrium

conditions the reaction was initiated by turning down the central shaft which lowered the baffle plates and crushed the glass ampoule. All runs were performed adiabatically. The evolved hydrogen was confined within the bomb during each of the runs.

RESULTS

From the amounts of materials used, the following equations represent the reactions studied:

$$Al + 60(HCl \cdot 14H_2O) \longrightarrow (AlCl_3 + 57HCl) \cdot 840H_2O + 3/2H_2$$

$$Li + 60(HCl \cdot 14H_2O) \longrightarrow (LiCl + 59HCl) \cdot 840H_2O + 1/2H_2$$

$$Li_3AlH_6 + 60(HCl \cdot 14H_2O) \longrightarrow (3LiCl + AlCl_3 + 54HCl) \cdot 840H_2O + 6H_2$$

Heats of reaction at constant volume, ΔE, were converted to their corresponding constant pressure values by the equation:

$$\Delta H = \Delta E + \Delta nRT$$

Tables II and III present the experimental data. Run Li-9 shows no measurable effect by doubling the sample weight. Runs Al-10 and Al-11 were made in 4 N HCl containing lithium ions at a concentration equal to that following a lithium run. No significant difference is noted when compared with aluminum runs made in the absence of the lithium ions. The possibility of interaction at these dilutions is shown to be negligible.

From the measurements of the heats of solution, the heat of formation of Li_3AlH_6 was calculated:

	$\Delta H_{reac.}$ kcal/mole
ΔH_1: 1x[Al + 3HCl(aq) ---> $AlCl_3$(soln) + 3/2H_2]	-128.14 $\pm$ .39
ΔH_2: 3x[Li + HCl(aq)---> LiCl(soln) + 1/2H_2]	(3x) - 67.05 $\pm$ 0.53 = -201.15 $\pm$ 1.6
ΔH_3: 1x[Li_3AlH_6 + 6HCl(aq) ---> ($AlCl_3$ + LiCl)(soln) + 6H_2]	-249.89 $\pm$ 1.47

3Li + Al + 3H_2 ---> Li_3AlH_6

$\Delta Hf_{298°}$ Li_3AlH_6 = $\Delta H_1 + \Delta H_2 - \Delta H_3$

= -79.39 $\pm$ 3.45 kcal/mole

All uncertainties listed in this work are twice the standard deviation, or 2σ, according to Rossini[2].

DISCUSSION

Upon receiving the Li_3AlH_6 from Reaction Motors, four samples were prepared in our vacuum dry box for preliminary calorimetric runs. No samples were taken at this time for concurrent chemical analysis. The heats of reaction of these four runs as shown in Table IV were higher than the second batch of samples used in runs 5 to 11. During the preparation of this second batch of samples, material was also prepared for the analytical

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[2] F.D.Rossini, Chemical Reviews 18, 233 (1936)

work, the results of which were utilized in this work. It appears that the material was in a higher purity state at the first sampling, but that either with time, or accidental sampling contamination, the purity of the second sampling was lessened.

APPENDIX I

APPARATUS

The heats of solution were measured in a modified Parr combustion calorimeter operated adiabatically (see Figure 1). The bomb (see Figure 2) consisted of a nickel alloy body, the inner wall of which was gold-plated. A special lid was constructed through which passed a centered, gas-tight, moveable shaft. Two baffle plates were attached to the bottom section of the shaft which allowed the sample (contained in a glass vial) to be crushed while submerged in the acid. The plates further prevented splattering resulting from violent reactions. A thin tantalum sheet was placed on the bottom of the bomb. The bottom plate was constructed of tantalum, also. The lid bottom, shaft, and upper baffle were also gold-plated for protection against attack by the acid. A relief valve was also built into the lid to exhaust the bomb prior to a run and to release hydrogen following the run.

The lid to the calorimeter jacket was modified to allow the crushing shaft, thermistor tube, and heater tube to pass through to the calorimeter bucket contained within. Beckmann thermometers were used to monitor the bucket and jacket water temperatures. Improvements in water circulation were made by increasing the rate of stirring (small pulley used) and by placing a tube around the stirrer blades.

CALORIMETER

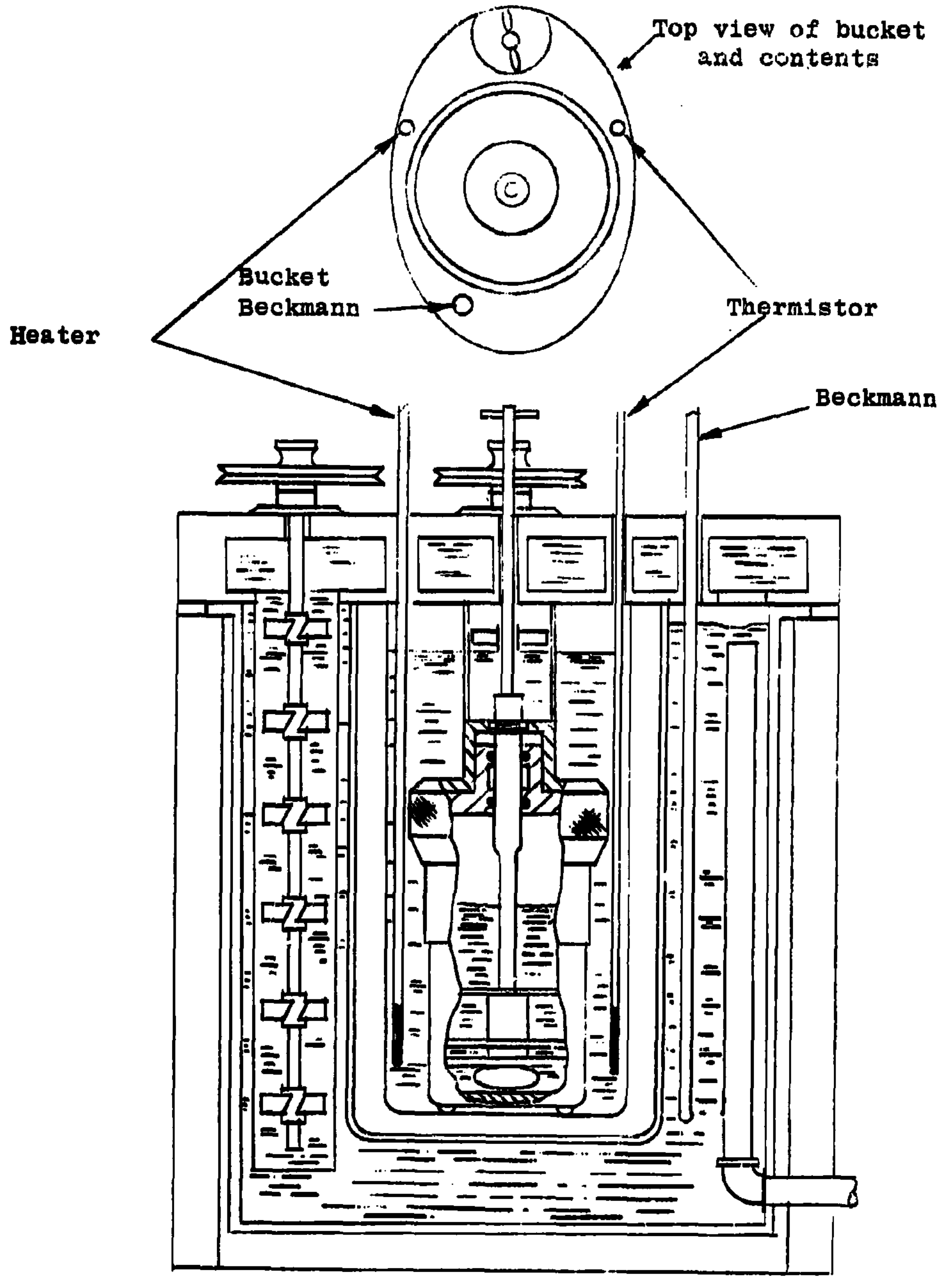
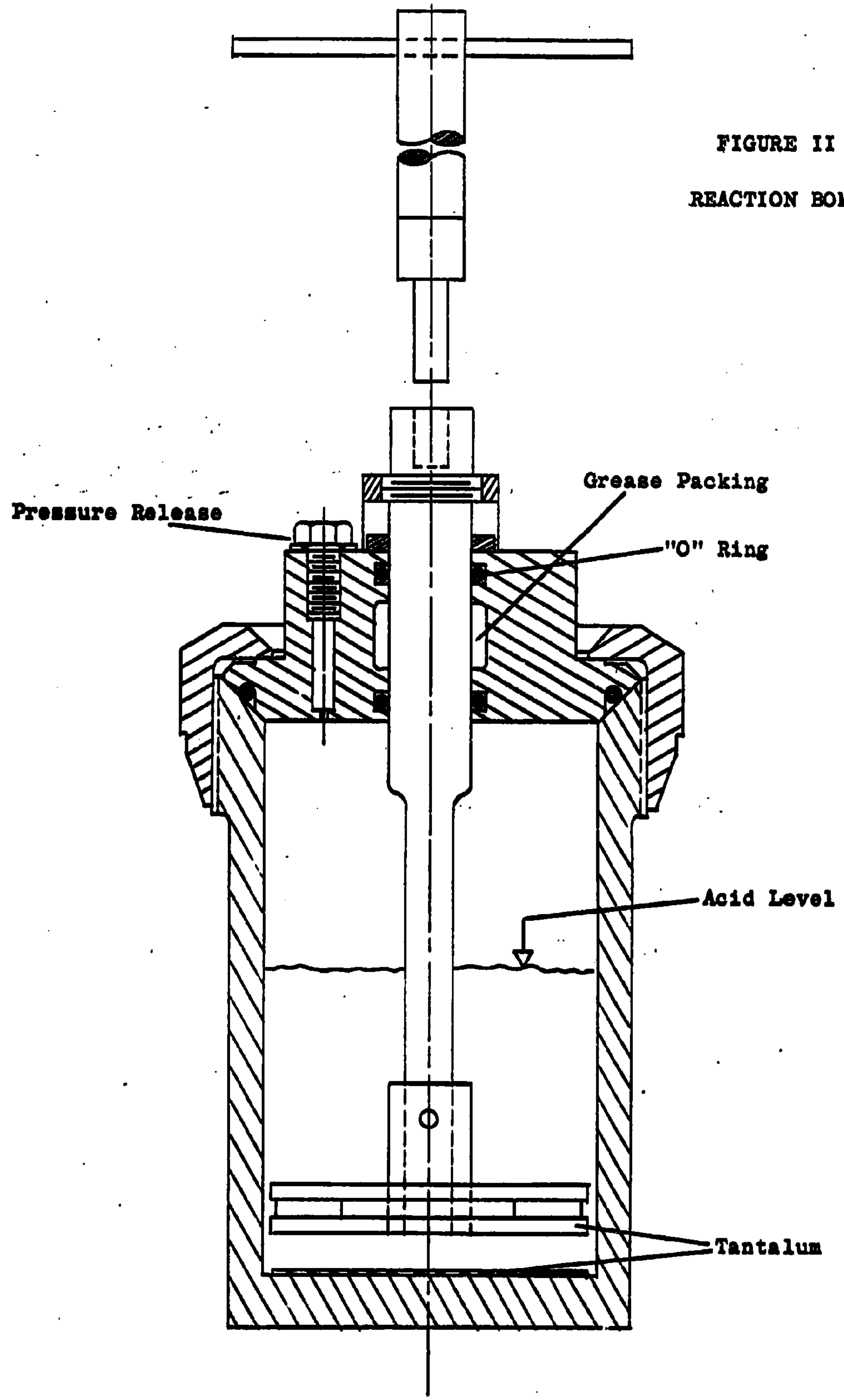


FIGURE I

FIGURE II

REACTION BOMB



APPENDIX II

MATERIALS

Lithium --

The lithium metal was obtained from Lithium Corporation of America as 99.9% lithium.

Spectrographic Analysis of Lithium

Element sought	Found (ppm)
Fe	1
Ni	<1
Cr	<1
Al	<10
Ti	ND<1
Cu	<5
Ca	10
Mg	10
V	ND<1
Pb	ND<5
Sn	ND<1
Mn	<1
Co	ND<10

Aluminum --

The aluminum wire was obtained from Mallinkrodt Chemicals.

Element sought	Found (ppm)
Ni	0<10
Ti	0<10
Fe	10
Cr	<10
Mg	<10
Mn	ND<5
Si	10
B	ND<10
V	ND<10
Cu	<10

Li-Al-H

The sample was obtained from Reaction Motors Division of Thiokol Chemical Corporation. The material was analysed as follows:

aluminum - EDTA
lithium - flame photometer
hydrogen - evolution by reaction with HCl
chlorine - volumetric

Results

% Al	% Li	%LiCl	% H	
45.70	37.39	--	--	
45.60	37.72	--	--	
45.59	37.51	--	--	
45.45	37.84	--	--	
45.77	38.01	--	9.82	
45.77	37.67	1.79 (0.29% Li)	9.84	
45.65	37.68	1.79 (0.29% Li)	9.83	Averages

The % Li as LiCl, when subtracted from total lithium yields 37.39% lithium in the Li-Al-H compound.

The purity of the compound Li-Al-H equals 92.87%. The stoichiometry was determined as follows:

	%	Moles	Molar ratio based on Li	Al	H_2	Average
Li	37.39	5.39	3.00	3.19	3.31	3.17
Al	45.65	1.69	0.94	1.00	1.03	0.99
H	9.83	9.75	5.45	5.77	6.00	5.74

The material was, therefore, assigned the formula: Li_3AlH_6.

TABLE I

ELECTRICAL CALIBRATIONS

q, cal.	ΔR, ohms	$E = \frac{q}{\Delta R}$, cal/ohm
529.68	16.438	32.22
577.54	17.972	32.14
554.80	17.093	32.46
563.09	17.384	32.39
568.91	17.562	32.39
		32.32 $\pm$ .119* Average

*Uncertainty calculated as twice the standard deviation = 2σ

TABLE II

HEAT OF REACTION OF ALUMINUM WITH 4N HCl

Run No.	m, gm	$\Delta R, \Omega$	E, cal/Ω	$E.\Delta R-c_{pt}$*	$-\Delta E_{298}$ cal/mole	$-\Delta H_{298}$ cal/mole
Al-4	0.2404	31.909	36.03	1147.2	128757	127869
Al-5	0.2398	31.812	36.03	1143.7	128685	127797
Al-6	0.2696	36.010	36.03	1294.9	129593	128705
Al-7	0.2700	36.067	36.03	1297.0	129611	128723
Al-9	0.2701	35.971	36.03	1293.5	129213	128325
Al-10	0.2719	363.04	36.03	1305.5	129549	128661
Al-11	0.2707	36.034	36.03	1295.8	129156	128268
Al-12	0.2703	36.111	36.03	1296.1	129377	128489
Mean						128230
Mean - C_{break}						128140
Uncertainty						266
%						0.21

HEAT OF REACTION OF LITHIUM WITH 4N HCl

Run No.	m, gm	$\Delta R\ \Omega$	E, cal/Ω	$E.\Delta R-c_{pt}$	$-\Delta E_{298}$ cal/mole	$-\Delta H_{298}$ cal/mole
Li-1	0.0696	18.764	35.97	674.9**	67286	66990
Li-2	0.0777	20.935	35.97	753.0**	67247	66951
Li-3	0.0768	20.758	35.97	746.7**	67465	67169
Li-7	0.0835	22.911	35.97	824.1**	68484	68188
Li-8	0.0954	25.446	35.97	915.3**	66575	66279
Li-9	0.1395	37.701	36.03	1358.4**	67569	67273
Mean						67142
Mean - C_{break}						67052
Uncertainty						516
%						0.77

*c_{pt} = Catalyst Correction = 2.5 cal/0.17 gm H_2PtCl_6 (10% solution)

**No catalyst used.

TABLE III

HEAT OF SOLUTION OF Li_3AlH_6

Run	m, gms	$\mathcal{E}\Delta R^*$ cal	$-\Delta E$ kcal/mole $\frac{\mathcal{E}\Delta R\, M}{m}$	$-\Delta H$ kcal/mole Unc**	$-\Delta H$ kcal/mole corr.
8B	0.1270	556.03	235.765	232.195	250.021
9B	0.0906	399.53	237.469	233.899	251.855
10B	0.1028	449.24	235.326	231.756	249.548
11B	0.1033	455.77	237.592	234.022	251.988
12B	0.1095	475.78	233.879	230.409	248.098
13B	0.1073	467.53	234.636	231.066	248.805
14B	0.1099	479.14	234.774	231.204	248.954
				Average	248.896 $\pm$ 1.47***

*Corrected for heat of breaking glass capsules = 0.9 cals, 4 drops of 10% solution of $H_2Pt + Cl_6$ catalyst = 2.5 cals

**Uncorrected in respect to purity

***Uncertainty calculated as twice the standard deviation = 2σ

$\mathcal{E}$ = 32.32 cal/ohm

M = 53.850

$\Delta H = \Delta E + \Delta nRT$, where ΔnRT = 3.57 kcal

TABLE IV

HEAT OF SOLUTION OF Li_3AlH_6 (FIRST SAMPLING)

Run	m, gms	$\frac{\mathcal{E}\Delta R^*}{cal}$	$-\Delta E$ kcal/mole $\frac{\mathcal{E}\Delta R\,M}{m}$	$-\Delta H$ kcal/mole Purity unknown
2B	0.1025	459.10	241.195	237.625
3B	0.0961	430.53	241.249	237.679
4B	0.1039	467.57	242.335	238.765
6B	0.0865	386.77	240.781	237.211
			Average	237.820 ± 0.664**

*Corrected for heat of breaking glass capsule = 0.9 cals,
4 drops of 10% solution of $H_2Pt \div Cl_6$ catalyst = 2.5 cals

**Uncertainty calculated as twice the standard deviation = 2σ

$\mathcal{E}$ = 32.32 cal/ohm

M = 53.850

$\Delta H = \Delta E + \Delta nRT$, where ΔnRT = 3.57 kcal

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